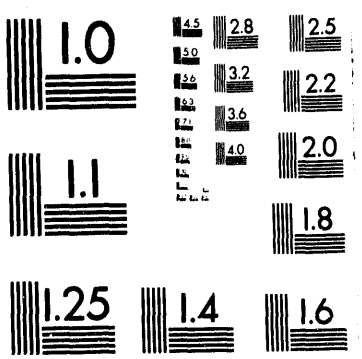
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QUARTERLY TECHNICAL PROGRESS REPORT 4
JULY - SEPTEMBER, 1993

DEVELOPMENT OF VANADIUM-PHOSPHATE CATALYSTS FOR METHANOL PRODUCTION BY SELECTION OXIDATION OF METHANE

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EXECUTIVE SUMMARY

This document is the fourth quarterly technical progress report under Contract No. DE-AC22-92PC92110, "Development of Vanadium-Phosphate Catalysts for Methanol Production by Selective Oxidation of Methane". During this quarter, we tested a VPO catalyst prepared in aqueous reaction media and compared the results obtained with those reported last quarter for an organic media preparation. The catalyst prepared in organic media was much more active and much more stable under reaction conditions. Analysis of the fresh and used catalysts has revealed that the activation procedure employed (activation in wet nitrogen) led to a loss of phosphorus from the catalyst, and this may contribute to the poor selectivity observed. Also, activation of the aqueous catalyst in this way did not lead to the formation of $(VO)_2P_2O_7$ as desired but led to β-$VOPO_4$. This compound is not known as a selective oxidation catalyst.

Future tests will employ catalysts activated under dry conditions which do not cause a loss of phosphorus. Future tests will also utilize methane and oxygen diluted with helium. This will allow us to freely vary the methane-to-oxygen ratio without entering the flammable composition region. We plan to initially conduct a brief study to insure that our data are free of external mass transport limitations. Based on these results, we will select one feed gas flow rate. This will be followed by a test series in which temperature, pressure, and CH_4:O_2 ratio will be varied. A few tests where steam is included in the feed will be conducted. Also, catalyst effectiveness at converting methanol to other products will be examined. The catalyst used in these tests will be a VPO_{org} activated in dry gas such that the P:V is greater than 1.

A series of blank runs was conducted with methane and/or methanol as the reactant. The hydrocarbon-to-oxygen ratio was 2:1 and the feed gas contained 70 mole percent helium. The purpose of the runs with methanol was to define an operating range wherein homogeneous methanol conversion did not occur or occurred very slowly. These runs have indicated that the range of methanol stability is well matched with reasonable operating conditions for vanadium phosphate catalysts. Methane oxidation tests indicated that relatively high methanol selectivities could be obtained at very low methane conversion, in agreement with literature reports.

Preliminary work directed at preparing a silica supported vanadium phosphate catalyst has also been performed. Mixing of the precursor slurry or solid with silica produces a material which can be activated to produce $(VO)_2P_2O_7$. However, these are not truly supported catalysts. Impregnation of the silica with the precursor slurry and activation following a procedure outlined in the literature resulted in the formation of unidentified VPO compounds. We plan to continue this work using more conventional activation procedures for the impregnated catalysts. Also, several other catalyst supports are currently being prepared.

INTRODUCTION

This document is the fourth quarterly technical progress report under Contract No. DE-AC22-92PC92110, "Development of Vanadium-Phosphate Catalysts for Methanol Production by Selective Oxidation of Methane". During this quarter, we focused primarily on catalyst activity testing in the microreactor. Additional blank runs using methane and methanol were performed. Initial attempts at preparing a silica supported catalyst are described.

These results are discussed in detail below and plans for the coming quarter are outlined.

PROJECT DESCRIPTION

OBJECTIVES

The specific objectives of this project are to:

- Develop an economical catalyst for partial oxidation of methane to methanol.
- Determine optimum conditions for methanol production from methane using VPO catalysts.
- Utilize promoters and catalyst supports to improve methanol yield relative to the base case catalysts.
- Provide a preliminary understanding of how these promoters and supports actually affect catalyst properties.
- Use the information obtained to prepare advanced catalysts which will be tested for activity, selectivity, and stability.
- Develop a simplified methanol production process flowsheet based on these advanced catalysts.

PROJECT OVERVIEW

Under the project entitled "Development of Vanadium-Phosphate Catalysts for Methanol Production by Selective Oxidation of Methane", Amax R&D is performing laboratory scale development of a promising, practical catalyst for the selective oxidation of methane to methanol. The primary component of this catalyst is vanadium-phosphate (VPO) which has shown good activity and selectivity in the partial oxidation of n-butane and propane but has not been studied in detail for methane oxidation.

The goal of the project is to develop a catalyst which allows methane oxidation to methanol to be conducted at high conversion and selectivity. Ideally, a low CH_4/O_2 ratio will be employed with air as the source of oxygen. Initially, some tests are being conducted under more conventional conditions of 90 to 95 percent methane, with the balance oxygen. Temperatures below 600°C and pressures up to 20 atm are to be investigated. The use of steam in the feed gas will also be investigated. The catalyst development strategy will be to utilize promoters and supports to improve the activity and selectivity of the unmodified VPO catalyst. Catalysts will be characterized by nitrogen adsorption/desorption, elemental analysis, X-ray powder diffraction, and FTIR.

The project is divided into four tasks:

- Task 1. Laboratory Setup

  Equipment for catalyst preparation and reactivity testing was set up and tested. Gas analytical procedures were developed. Blank reactor runs were conducted. This task was completed at the end of December 1992.

- Task 2. Process and Catalyst Variable Study

  Tests are being conducted to determine the optimum conditions of temperature, pressure, CH_4/O_2 ratio, H_2O/CH_4 ratio, space velocity, and catalyst P:V ratio for high activity and selectivity in methanol production. This task is ongoing and should be completed by the end of November 1993.

- Task 3. The Effect of Promoters and Supports

  Several promoters and supports will be tested. The measured response will be activity and selectivity in the methane oxidation reaction to methanol. Catalyst characterization will provide a fundamental understanding of these effects. This task is slated to begin in October 1993, and preliminary work on preparing a supported catalyst is described in this report.

- Task 4. Advanced Catalyst Testing

  Advanced catalysts which are both promoted and supported will be prepared. These catalysts will be tested in runs of relatively long duration (200 hours) to determine long-term activity, selectivity, and stability in methane oxidation to methanol. This task is slated to begin in August 1994.

PROJECT STATUS

CATALYST TESTING

Catalyst testing is performed in a quartz-lined microreactor system which has been described in previous reports.

Tests Using $(VO)_2P_2O_7$ - Aqueous Preparation

The catalyst employed was prepared using the following procedure. Fifteen grams of V_2O_5 were dissolved in 37 percent aqueous HCl. The solution was stirred and refluxed for 3 hours. Phosphoric acid (22.8 grams) was then added, yielding a P:V ratio of 1.2, and refluxing was continued for another 2 hours. The solution was poured into a beaker and water was evaporated overnight at 150°C, yielding a light blue solid. This blue solid was then washed in boiling water for 1 hour and air dried at 150°C for 24 hours. The precursor obtained in this way exhibited an X-ray diffraction pattern closely matching that of the desired precursor $VO(HPO_4)$-0.5 H_2O (Johnson et al., 1984). The P:V ratio of this material was 0.90.

The catalyst precursor powder was pressed into a tablet using a hydraulic press and a pressure of 20,000 psi. These tablets were broken and screened to 0.84 by 1.41 mm. To activate, the sample was heated in air to 380°C at 3°C/ minute and held 4 hours. The gas was then switched to nitrogen which was passed through a bubbler where it was saturated with moisture. The temperature was increased to 500°C at 3°C/minute and held for 16 hours. X-ray diffraction results for this catalyst indicated that it was highly crystalline β-$VOPO_4$. The P:V ratio had decreased from 0.90 to 0.87. A bed volume of 1 to 2 cm^3 was employed in these tests which required a catalyst mass of 0.2 to 1.0 gram. The reaction gas was 93 percent methane with the balance oxygen.

Results are listed in Table 1 for the aqueous HCl catalyst (VPO_{aq}). Oxygen conversion was less than 100 percent in all cases. Carbon balances ranged from 98 to 102 percent. Calculation of oxygen balances is also important but was not performed for these runs. Future work will include oxygen balances. Carbon oxides are the only products observed under these conditions.

The VPO_{org} catalyst was much more active than VPO_{aq} or V_2O_5/SiO_2, as shown in Figure 1 where conversion is plotted as a function of temperature under otherwise identical conditions. Results for blank runs are also included and indicate that homogeneous conversion of methane is very low. It should be noted that the surface area of the silica supported catalyst is 160 m^2/g, while that of the VPO catalysts is in the range of 20 to 40 m^2/g.

Table 1. Results of Methane Oxidation Run Using $(VO)_2P_2O_7$ Prepared in Aqueous HCl

Nominal Temperature °C	Pseudo-Contact Time, mg-min/ml	% CH_4 In.	% Conversion	% Selectivity CO	% Selectivity CO_2
450	12	93	0.12	66	34
475	12	93	0.40	66	34
500	12	93	0.57	73	27
550	12	93	2.35	47	53

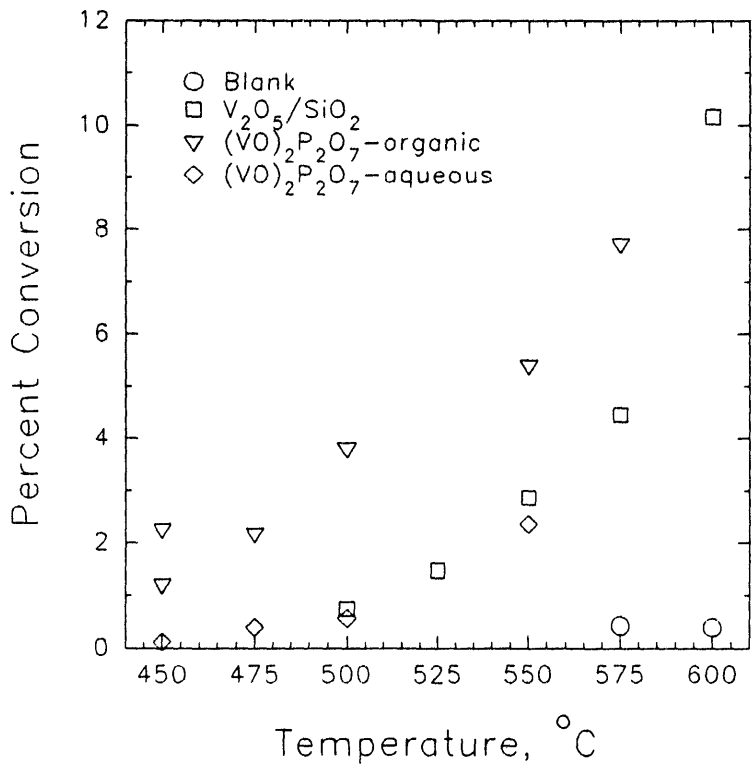

Figure 1. Conversion as a function of temperature for methane oxidation over VPO and V_2O_5/SiO_2 catalysts at 1 atm, 93 percent CH_4, and 12 mg-min/ml pseudo-contact time.

Carbon monoxide selectivity as a function of temperature is plotted in Figure 2 for these catalysts. The VPO_{org} catalyst produces almost exclusively CO, while considerable CO_2 is observed over VPO_{aq} and V_2O_5/SiO_2. Referring to the reaction pathway shown in Figure 2, this high CO selectivity suggests that a reaction pathway which includes selective intermediates is operative on VPO_{org}. Alteration of

reaction conditions or promotion of the catalyst might, therefore, allow these selective products to be observed in the product gas. Also, it is important to note that the steam activation procedure used for these catalysts was not optimum. For the aqueous preparation, the P:V ratio was already low (0.90), and after activation, it was essentially the same at 0.87. However, activation of this catalyst in wet gas did not produce the desired active phase. For the organic preparation, the precursor P:V was 1.07 and steam activation reduced this to 0.97. This loss of phosphorus may account for the low selectivity observed (Hodnett, 1985; Horowitz et al., 1988).

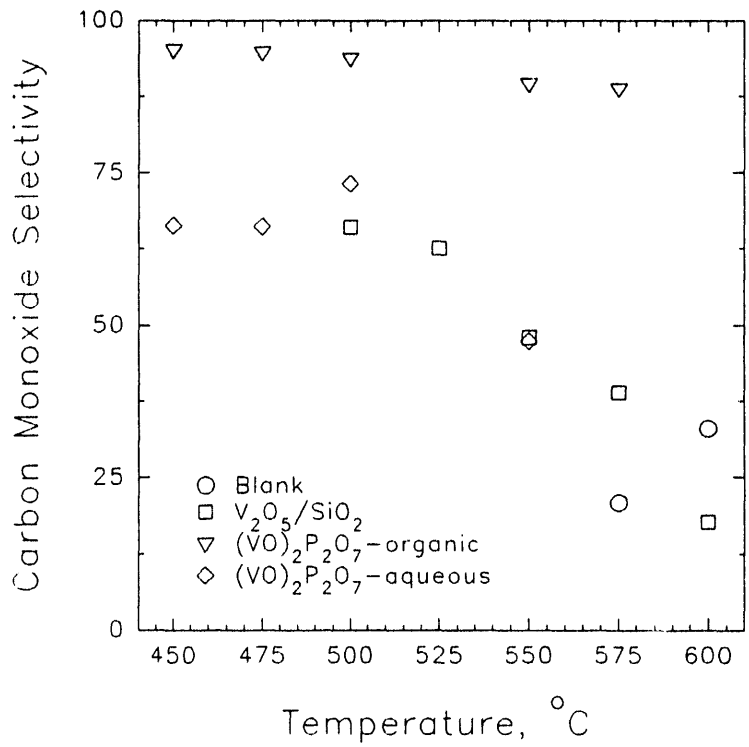

Figure 2. Carbon monoxide selectivity as a function of temperature for various catalysts, reaction conditions as in Figure 1.

Characterization of Used Catalysts

Characterization results were reported in the last quarterly for the VPO_{org} catalyst. X-ray diffraction indicated that the catalyst was stable up to 500°C. Further characterization has shown that the catalyst retains the $(VO)_2P_2O_7$ structure up to 575°C under reaction conditions. The P:V ratio of the used catalyst was 0.99, essentially unchanged from that of the starting material (0.97).

Characterization of the used VPO_{aq} catalyst indicated no change from the starting material. X-ray diffraction showed the presence of β-$VOPO_4$ and the P:V ratio was 0.85.

These results indicate that the VPO_{aq} catalyst does not activate to form the desired catalyst. Also, the VPO_{org} catalyst which did form the desired precursor phase upon activation experienced a loss of phosphorus. This is consistent with other observations that vanadium phosphate stability is reduced in the presence of steam. For example, preliminary results using high partial pressures of steam (at elevated total pressure) indicate that the VPO_{org} catalyst transforms to β-$VOPO_4$ under these extreme conditions. Future tests will not use the steam activation procedure and care will have to be taken during tests including steam in the feed gas.

BLANK RUNS USING METHANE AND METHANOL

Recently we have revisited operation of our quartz-lined microreactor system as a non-catalytic reactor. Feed gases containing methanol or methane, as well as oxygen and helium, were employed. In all tests, the hydrocarbon-to-oxygen ratio was 2:1 and the feed gas contained 70 mole percent helium. Temperatures from 400 to 600°C and pressures from atmospheric up to 150 psig were investigated. Carbon balances were excellent in these runs, ranging from 99 to 101 percent. Oxygen balances were not as good and ranged from 85 to 107 percent. The reason for poor oxygen balances in some runs is thought to be a minor GC malfunction. This malfunction changed the retention time of the formaldehyde peak so that in some runs it was not observed. The problem has been solved and hopefully can be avoided in future runs.

Results for these blank reactor tests are listed in Table 2. The goal of the methanol oxidation tests series was to define a range of temperatures and pressures where non-catalytic methanol oxidation did not occur or occurred at a slow rate. The nominal reactant residence time in these tests was in the range of 2 to 6 seconds. Figure 3 shows the region of temperatures and pressures where methanol conversion was very low or zero. At atmospheric pressure, methanol was stable up to 550°C. As pressure was increased, lower temperatures were required. These results define the desired operating region from the standpoint of non-catalytic conversion of methanol to undesired products. Operation at temperatures and pressures not in the desired operating region could not possibly generate a high methanol selectivity. It is interesting to note that under some conditions, the primary product of methanol conversion is methane.

Non-catalytic methane conversion tests were conducted for two reasons. First, we wanted to know the extent of non-catalytic conversion at various conditions of temperatures and pressures. Secondly, we wanted to see if we could reproduce results reported in the literature for methanol production via this route.

Table 2. Results of Non-Catalytic Oxidation of Methane and Methanol

Temperature, °C	Feed Composition % He	% O_2	% CH_4	% CH_3OH	Pressure, psig	Residence Time, Seconds	% Conversion	% Carbon Balance	% Oxygen Balance	% Selectivity CO	CO_2	HCHO	CH_3OH	CH_4
550	70	10	20	0	0	0.47	0.00	99.50	–	0.00	0.00	0.00	0.00	–
600	70	10	20	0	0	0.44	0.00	99.60	–	0.00	0.00	0.00	0.00	–
400	70	10	20	0	100	3.92	0.00	100.14	–	0.00	0.00	0.00	0.00	–
450	70	10	20	0	100	3.65	0.00	99.93	–	0.00	0.00	0.00	0.00	–
500	70	10	20	0	100	3.41	0.11	100.24	–	78.11	21.89	0.00	0.00	–
550	70	10	20	0	100	3.20	49.52	100.11	85.28	61.75	24.30	0.00	13.94	–
525	70	10	20	0	100	3.30	45.85	99.92	85.60	55.64	18.21	0.00	26.16	–
500	70	10	20	0	75	2.56	0.06	100.46	100.56	0.00	100.00	0.00	0.00	–
550	70	10	20	0	75	2.40	1.33	100.31	101.09	21.27	37.82	0.00	40.91	–
500	70	10	20	0	150	5.11	0.81	100.05	101.78	5.36	16.63	0.00	78.01	–
525	70	10	20	0	150	4.95	56.46	107.70	99.33	65.34	16.09	0.25	18.33	–
525	70	10	0	20	0	0.49	0.24	100.04	99.71	14.14	53.94	31.92	0.00	–
550	70	10	0	20	0	0.47	0.27	99.67	99.97	22.23	12.86	0.00	0.00	64.8
550	70	10	10	10	0	0.47	2.19	102.91	98.46	1.07	0.58	0.54	0.00	97.8
600	70	10	10	10	0	0.44	13.46	100.19	100.26	62.76	8.94	28.31	0.00	–
450	70	10	20	0	225	8.20	0.00	99.38	100.80	0.00	0.00	0.00	0.00	–
500	70	10	20	0	225	7.67	31.13	100.33	100.51	63.48	23.35	0.89	12.3	–
550	70	10	0	20	75	2.40	80.31	99.81	46.49	84.24	10.49	0.86	0.00	4.4
525	70	10	0	20	75	2.48	96.57	100.88	96.11	49.05	50.30	0.00	0.00	0.7
500	70	10	10	10	75	2.56	2.90	99.66	100.14	1.34	0.53	1.07	0.00	97.1
490	70	10	10	10	150	5.18	45.20	102.63	107.90	41.20	4.02	0.00	0.00	54.8

As expected, higher methanol selectivities were obtained at low methane conversion. Increasing pressure lead to increased conversion at a given temperature. These results agree reasonably well with those reported by a number of research groups, although most reported results were obtained at higher temperature and pressure than employed here.

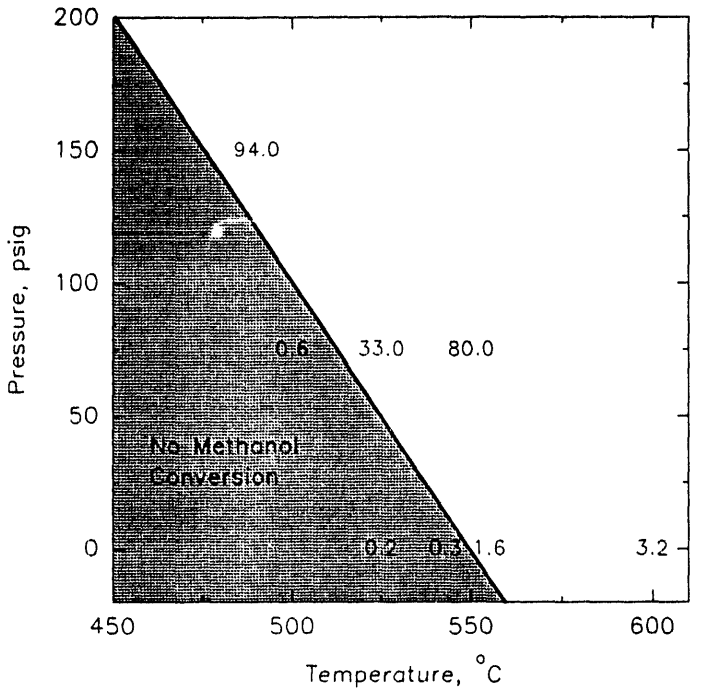

Figure 3. Non-catalytic methanol conversion as a function of temperature and pressure. Numbers on the plot indicate conversion.

A few runs were conducted using both methane and methanol in the feed. The results are not easy to interpret because it is not certain what reaction products formed from methane or from methanol. This is complicated by the fact that some of the methanol converts to methane. However, it does appear that methanol conversion is slightly higher in the presence of methane.

PREPARATION OF SILICA SUPPORTED CATALYSTS

Most active transition metal oxide catalysts for methane oxidation are supported on silica. In fact, some authors have suggested that the active sites for methane conversion are on the silica surface and are promoted by the transition metal oxide (Parmaliana et al., 1993). Preparing a VPO catalyst supported on silica is a challenging task. In earlier work, we have shown that the catalyst must be

prepared in organic media and properly activated to produce the stable active phase. The best method for adding a catalyst support to this preparation procedure is not obvious. To date, we have been investigating three methods:

- Mull-mixing of the solid catalyst precursor with silica.
- Mixing of the precursor/organic solvent slurry with silica.
- Impregnation of silica with the hot organic solution before precursor precipitation.

The silica employed in work performed to date is a commercially prepared, precipitated, and acid washed sample. Sodium and calcium contents of this silica are less than 100 ppm. Most samples were activated by heating at 3°C/minute in air to 380°C, holding for 4 hours, heating at 3°C/minute to 500°C in nitrogen, and holding for 16 hours.

Results of these preparations have been followed by X-ray diffraction. Figure 4 shows XRD patterns for the mull-mixed preparation both before and after activation. As would be expected, the precursor pattern shows the peaks of $VO(HPO_4)$-$0.5H_2O$ superimposed on the broad peak of the amorphous silica. Activation of this sample produces an incompletely activated $(VO)_2P_2O_7$, again superimposed on the broad silica peak. While this sample may not be a truly supported catalyst, it does appear that an intimate mixture of the active phase and silica can be prepared in this way.

Figure 5 shows XRD results for the catalyst prepared by mixing of the precursor slurry with the silica. The precursor sample exhibits only the peaks of the desired precursor phase; however, the intensities are highly skewed. In particular, the peak at 5.67Å is much more intense than expected. Activation of this sample produces a poorly crystalline $(VO)_2P_2O_7$. As for the sample discussed above, this preparation may not be a truly supported catalyst but an intimate mixture of silica, and the desired active phase can be prepared.

Only a small quantity of the impregnated silica was prepared, and all of it was activated by heating in air to 600°C. This procedure was selected based on a description in the literature of methods for preparing supported VPO catalysts (Kuo and Yang, 1989). Results of this activation are shown in Figure 6. The characteristic peaks of the active phase are not observed, indicating that this procedure will not work. Most likely the activation at 600°C is responsible for the failure of this procedure. In future work another impregnated sample will be prepared and activated using more conventional methods.

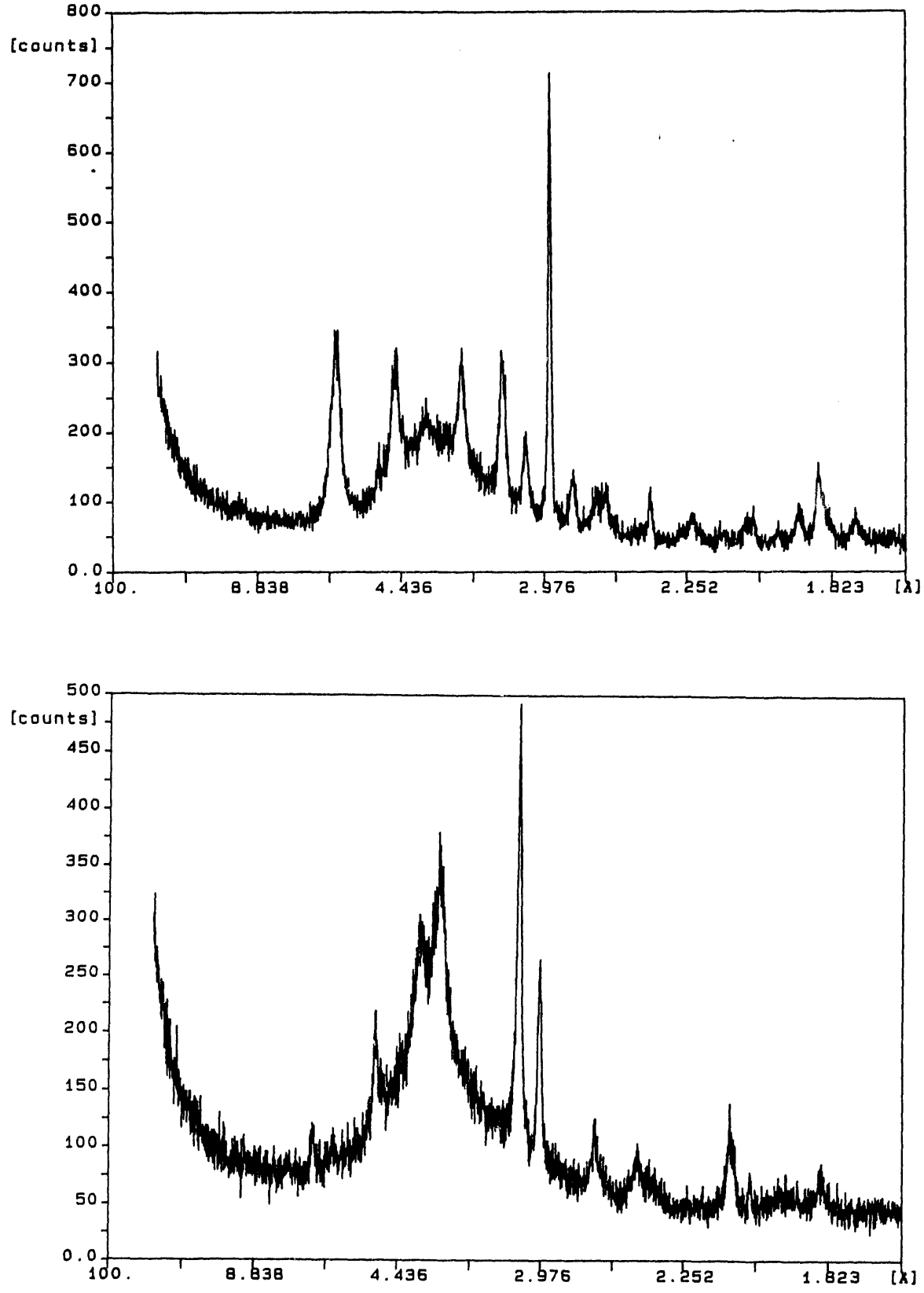

Figure 4. X-ray diffraction patterns for mull-mixing of catalyst precursor with silica. Starting mixture (top) and activated sample (bottom).

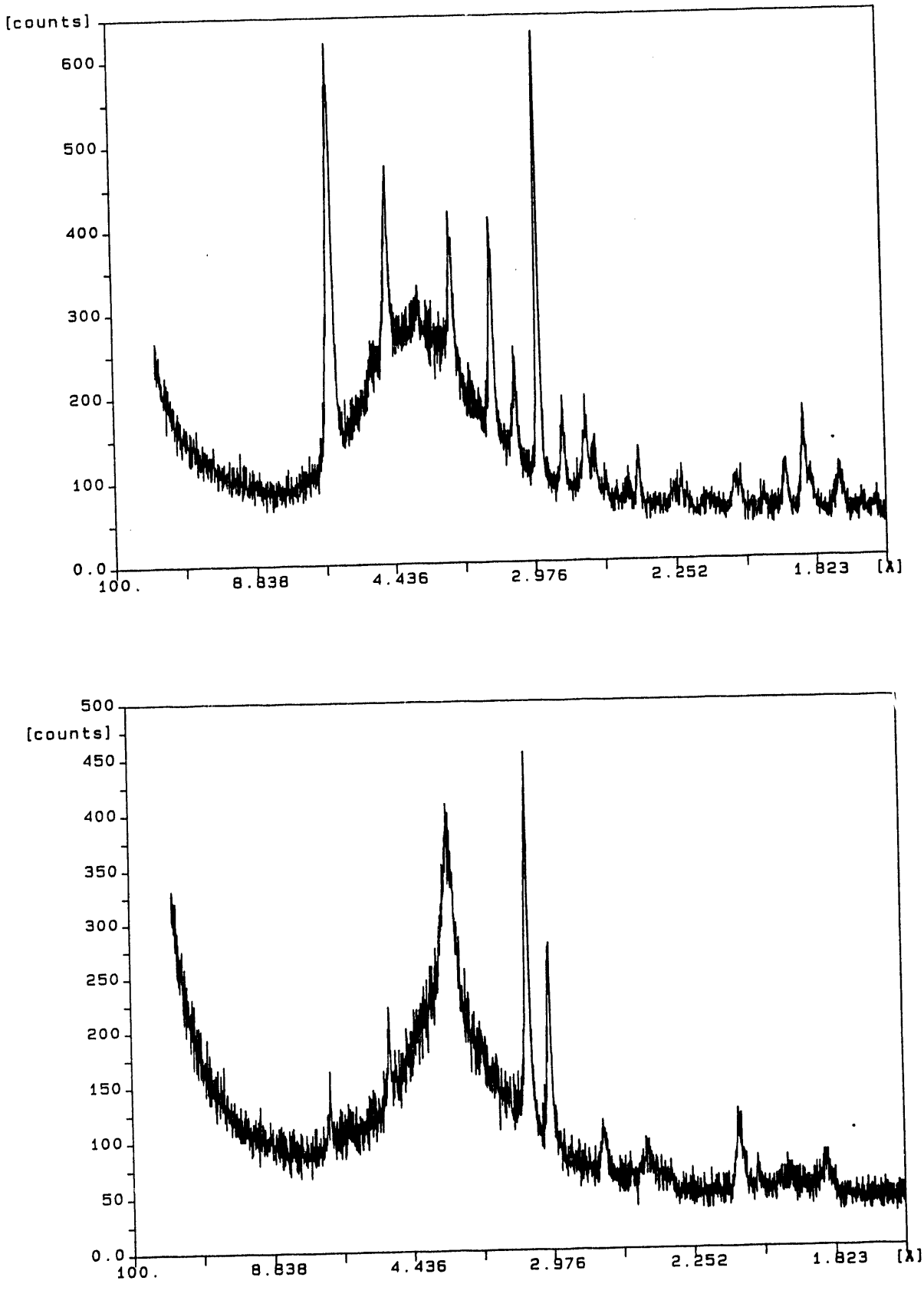

Figure 5. X-ray diffraction results for catalyst prepared by mixing of precursor slurry with silica support. Starting mixture (top) and activated sample (bottom).

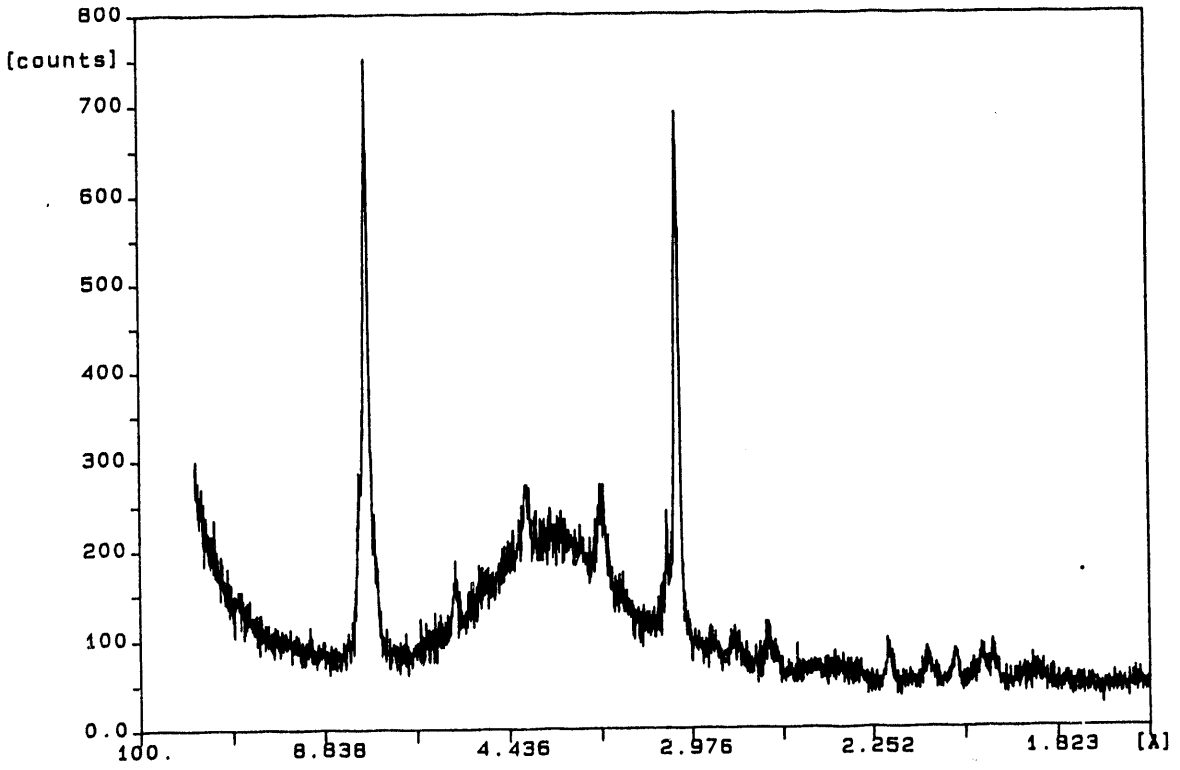

Figure 6. X-ray diffraction results for silica impregnated with hot precursor solution and activated at 600°C in air.

PLANNED ACTIVITIES

During the next quarter, our first priority will be to complete the work planned for Task 2, the catalyst and process variable study. Reaction conditions will be selected so that most tests are conducted in the region of no homogenous methanol conversion. A few catalytic methanol oxidation tests will also be conducted to determine if the catalyst rapidly converts methanol to other products. If this is the case, then the focus of our promoter and support study (Task 3) might be slightly altered towards finding promoters which reduce or eliminate methanol conversion. The catalyst used in the process variable study will be prepared in organic media and activated under dry conditions to have a high P:V ratio.

As a preliminary to completing this process variable study, we are performing a few tests to insure that our results are free of external mass transport limitations. The classical experiment of simultaneously varying flow rate (velocity) and bed volume to obtain a series of tests at identical residence time but increasing gas velocity will be employed. Based on the results of these tests, one gas velocity will be selected for all future tests.

We plan to continue our work in preparing supported catalysts and catalysts supports. By the end of the next quarter, preparation and characterization data for all of the supports which we plan to test will be available. Also, we hope to have found a good method for adding the VPO catalyst to the support.

SUMMARY

During this quarter, we tested a VPO catalyst prepared in aqueous reaction media and compared the results obtained with those reported last quarter for an organic media preparation. The catalyst prepared in organic media was much more active and much more stable under reaction conditions. Analysis of the fresh and used catalysts has revealed that the activation procedure employed (activation in wet nitrogen) led to a loss of phosphorus from the catalyst, and this may contribute to the poor selectivity observed. Also, activation of the aqueous catalyst in this way did not lead to the formation of $(VO)_2P_2O_7$ as desired but led to β-$VOPO_4$. This compound is not known as a selective oxidation catalyst.

Future tests will employ catalysts activated under dry conditions which do not produce a loss of phosphorus. Future tests will also utilize methane and oxygen diluted with helium. This will allow us to freely vary the methane-to-oxygen ratio without entering the flammable composition region. We plan to initially conduct a brief study to insure that our data are free of external mass transport limitations. Based on these results, we will select one feed gas flow rate. This will be followed by a test series in which temperature, pressure, and CH_4:O_2 ratio will be varied. A few tests where steam is included in the feed will be conducted. Also, catalyst effectiveness at converting methanol to other products will be examined. The catalyst used in these tests will be a VPO_{org} activated in dry gas such that the P:V is greater than 1.

A series of blank runs was conducted with methane and/or methanol as the reactant. The hydrocarbon-to-oxygen ratio was 2:1 and the feed gas contained 70 mole percent helium. The purpose of the runs with methanol was to define an operating range wherein homogeneous methanol conversion did not occur or occurred very slowly. These runs have indicated that the range of methanol stability is well matched with reasonable operating conditions for vanadium phosphate catalysts. Under some conditions, the primary product formed from methanol was methane. Methane oxidation tests indicated that relatively high methanol selectivities could be obtained at very low methane conversion, in agreement with literature reports. When methane and methanol were oxidized concurrently, conversions were slightly higher than observed for oxidation of each hydrocarbon separately.

Preliminary work directed at preparing a silica supported vanadium phosphate catalyst has also been performed. Mixing of the precursor slurry or solid with silica produces a material which can be activated to produce $(VO)_2P_2O_7$. However, these are not truly supported catalysts. Impregnation of the silica with the precursor slurry and activation following a procedure outlined in the literature resulted in the formation of unidentified VPO compounds. We plan to continue this work using more conventional activation procedures for the impregnated catalysts. Also, several other catalyst supports are currently being prepared.

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